Analysis of ACP Field Data Sets using Chemical Process Models: Results from Phoenix 1998

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Phoenix 1998 highlights

- An observed low ozone on May 20 and 21at the Usery pass surface measurement site operated by ANL during the experiment and its recovery on later days.
- Plumes containing high NOx measured at the Usery pass surface measurement site past midnight, ~every night. (paper discussing the possibility of HONO formation in these plumes conditionally accepted for publication in Atmos. Env.).

The May 20/21 low ozone episode

- Measured unusually low ozone(~30 ppb), CO (~150 ppb)at the surface site on the 20th
- Hydrocarbon measurements showed elevated CH3Cl(~900 pptv)
- On-site visual confirmation of a smoke(UV-b < 50%).
- Aircraft data from 21 shows a distinct and different trace gas signatures compared to 22.

Fig 1: TOMS aerosol index for May 19 1998 (from TOMS web site)_. Figure shows the diffuse smoke cloud from Mexico approaching Southwestern USA

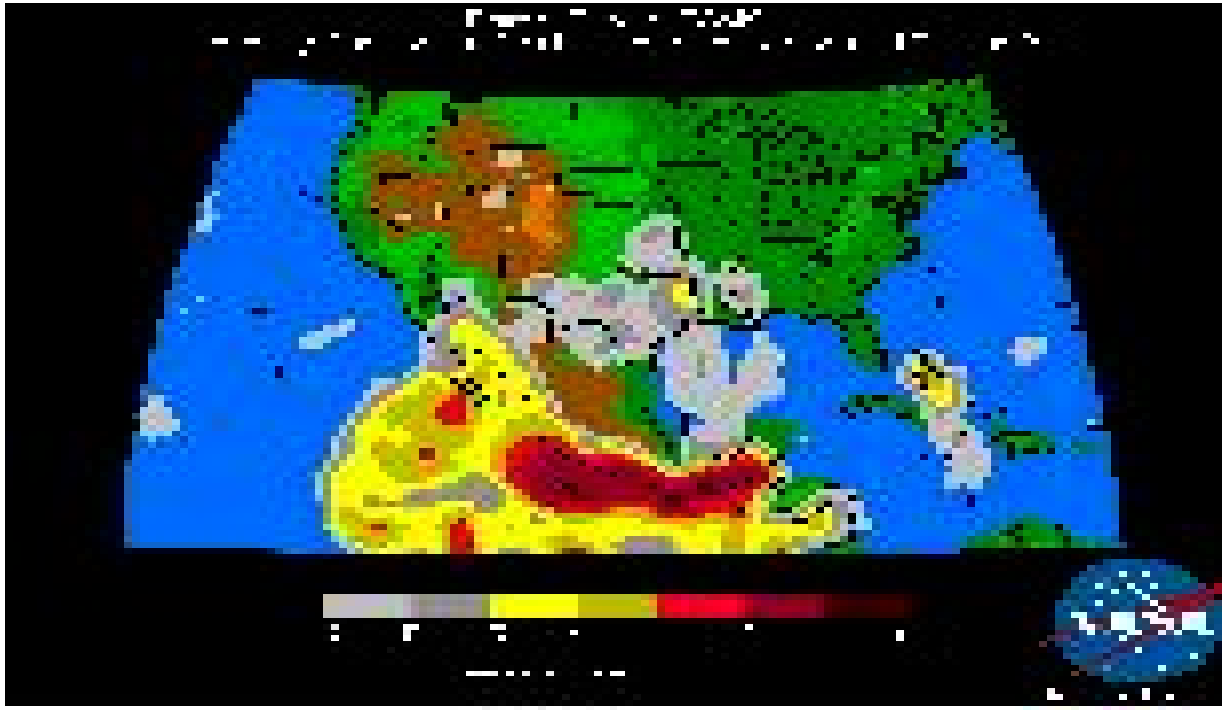
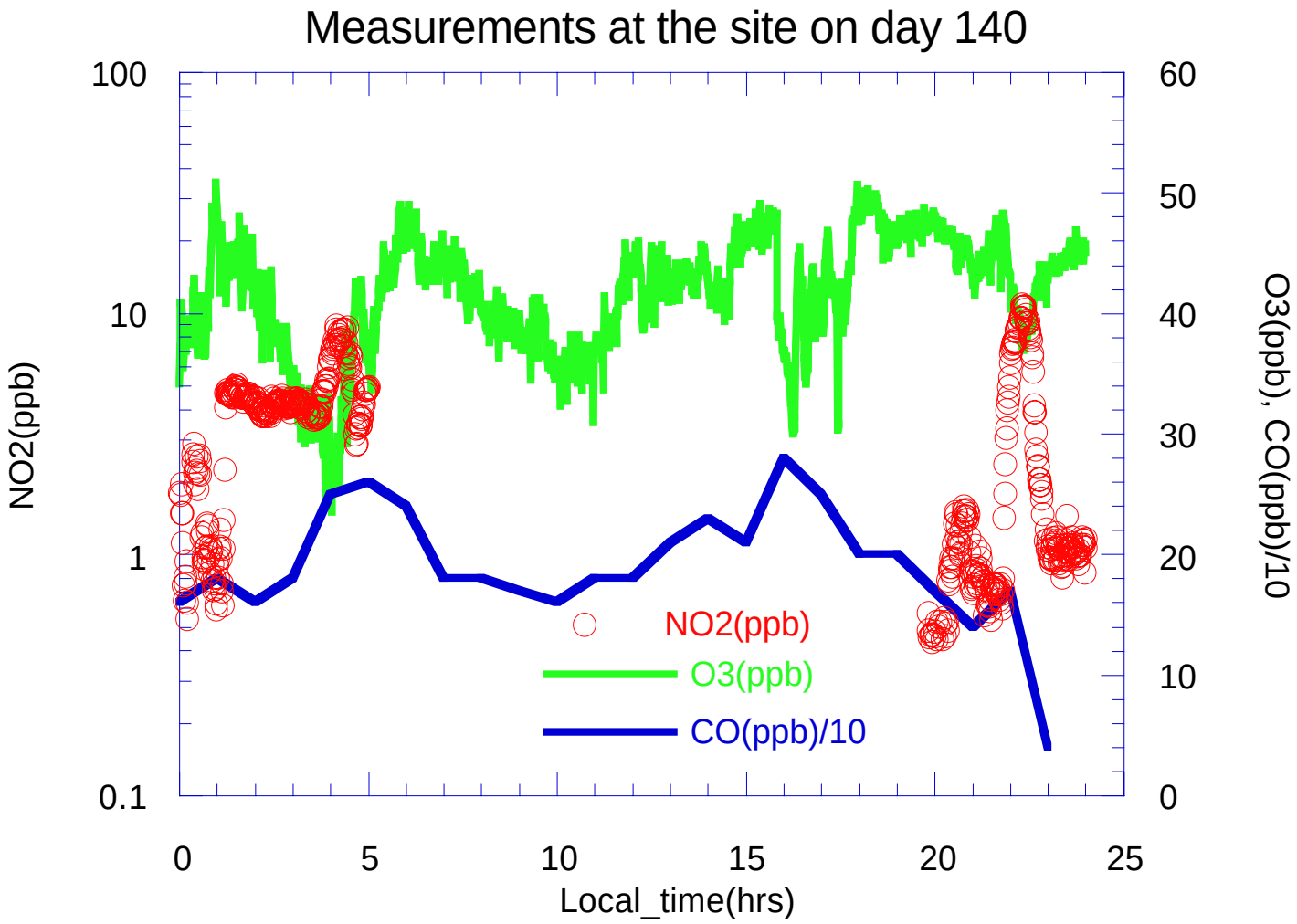
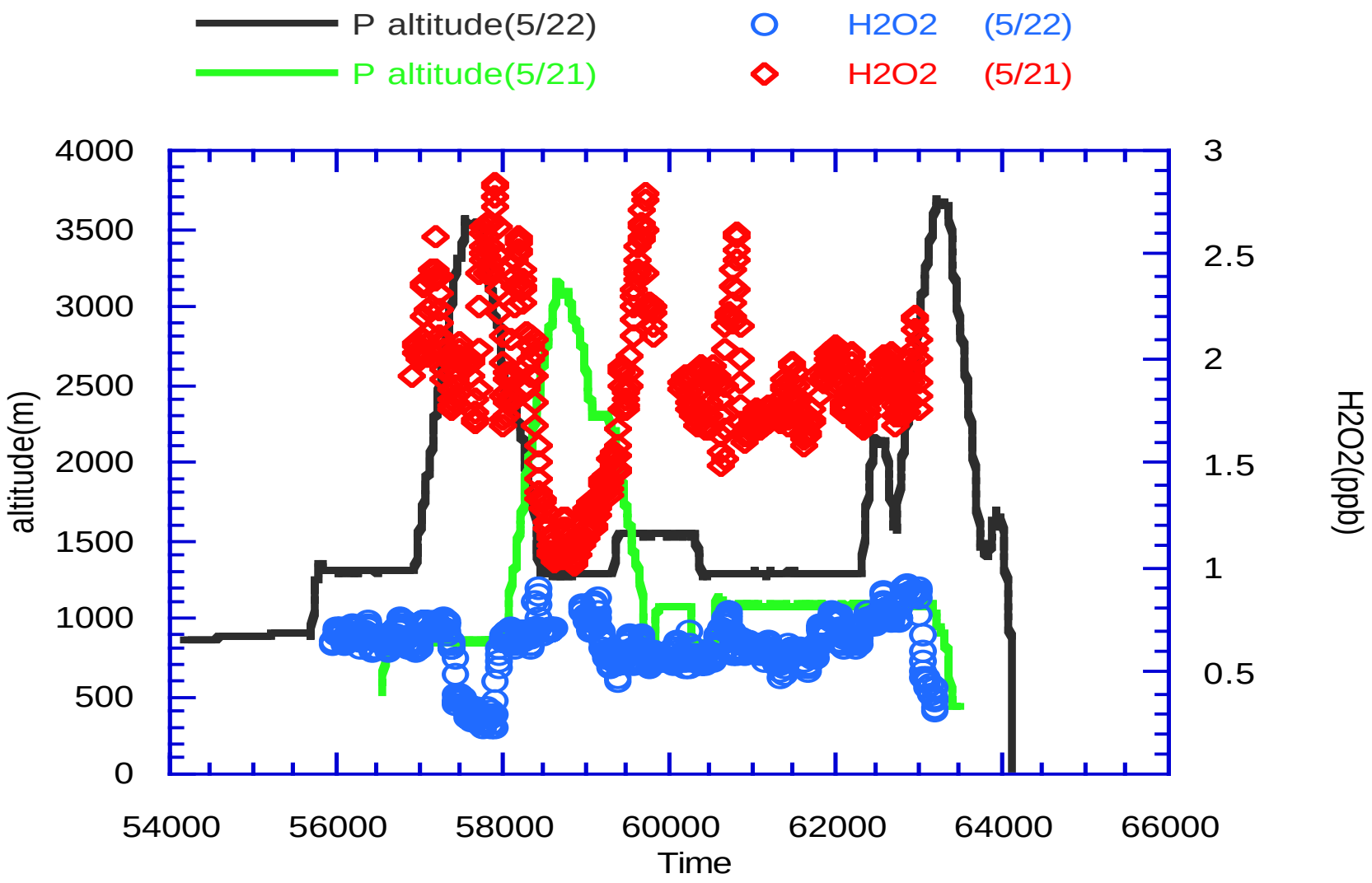


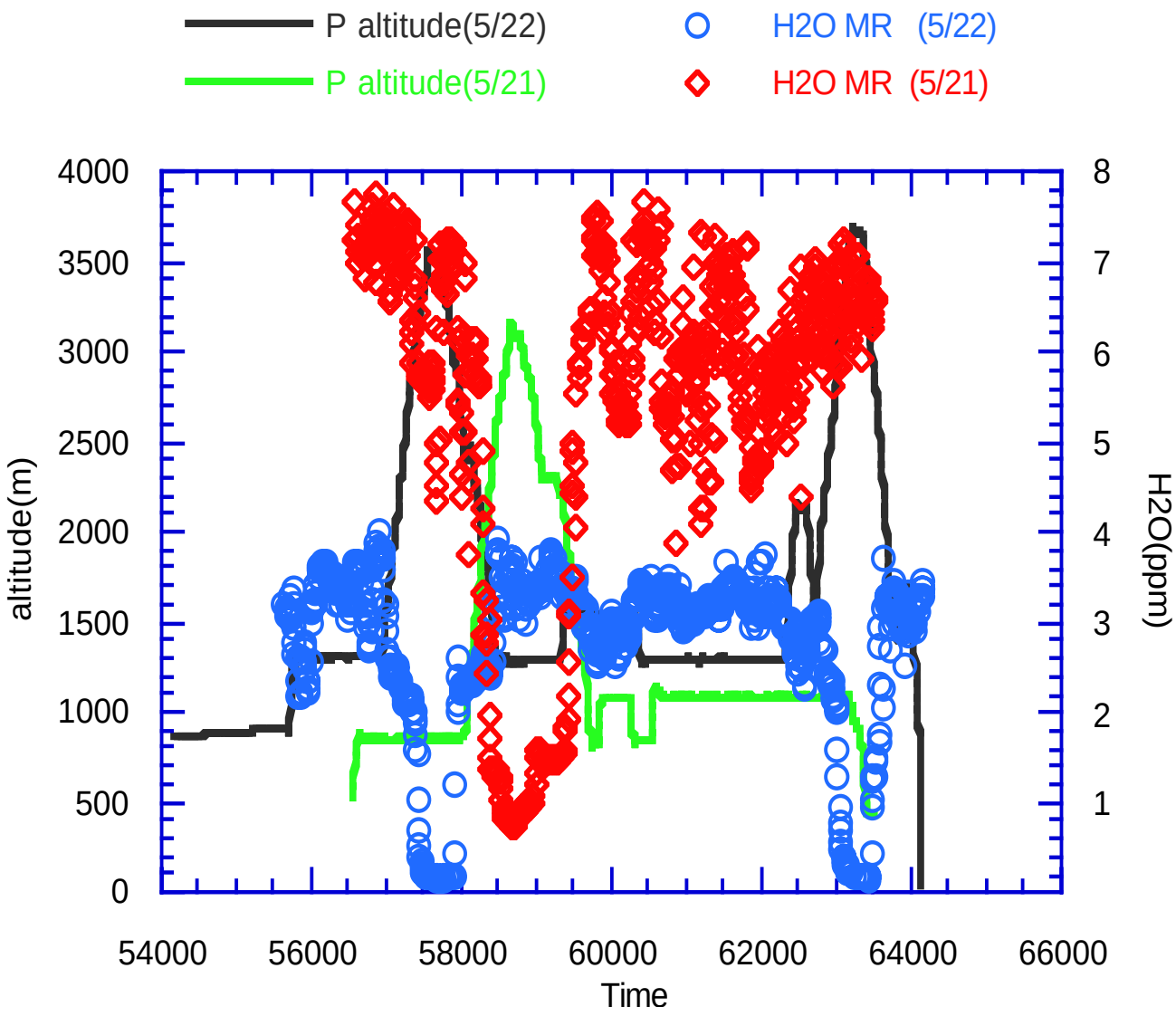
Figure 2 shows measured Ozone, CO and NO_2 on the day the smoke plume was observed in Phoenix from a surface site located in Phoenix.



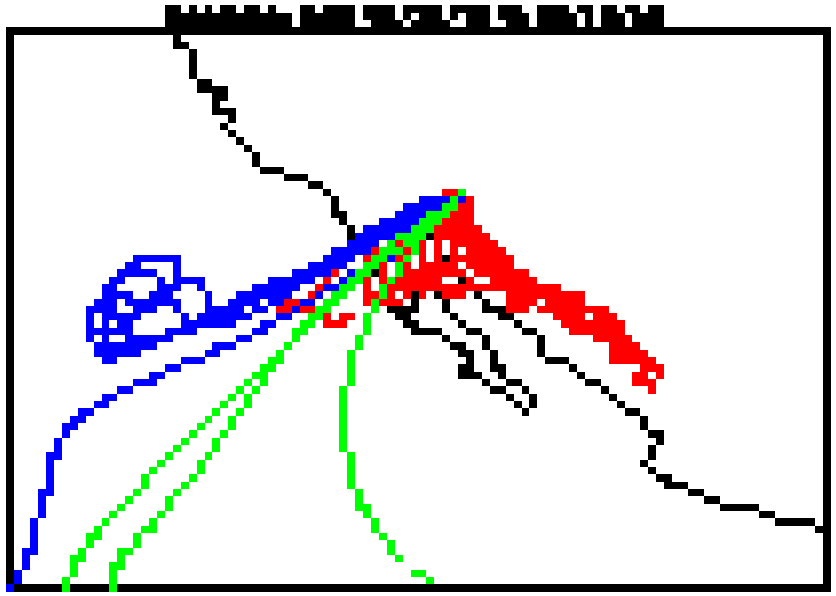
Measured H2O2 from the G-1 for May 21and 21.



Measurements of water vapor from the G-1 for May 21 and May 22



Backward trajectories reaching Phoenix on May 20 at 6 a.m. The red lines represent air below 850 mb, green line between 800 and 500 mb and blue lines above 500 and below 200 mb



Key Observations

- low ozone (30-40 ppb)
- high CH3Cl (~900 pptv)
- low NOx (the Arizona state dept reports 600 pptv of NO, which is their base line and around 1 ppb of NO2). No NO2 data from Jeff's group during this period .
- low CO (~ 150-200 ppb)
- up to 50% reduction in surface level UV-B at the Usery pass compared to previous days.
- higher water vapor (6000 ppm (30% relative humidity) compared to around 1000 ppm on a day after the event).
- High H2O2 and other peroxides on the day after the plume was observed at the surface site at the Usery pass (probably higher altitude air still coming from the forest fires on May 21), in the 2-3 km layer (above the boundary layer) in the G-1 measurements

- It is likely that the after the surface site at Usery pass experienced the event on May 20th, the air above the boundary layer was still coming from the forest fires on May 21. Usery pass started seeing clean air of possible marine origin from the afternoon of May 20. May 22 the aircraft measurements above the boundary layer show a marked change from May 21 and don't show any tell-tale signs of forest fires. Ozone levels, CO and H2O2 levels revert to more of a continental background mixing ratios.

Trajectory model

- 79 species
- 214 thermal and 32 photolytic reactions
- Two-stream multiple layer radiative transfer model
- several heterogeneous reactions included.
- HC chemistry scheme follows RACM mechanism with propane is however treated separately from lumped tracer HC3.
- Column ozone along the trajectory path from TOMS. 5 day calculations starting at 7.30 AM local time and ending 7.30 AM.

Plume Growth and initial conditions

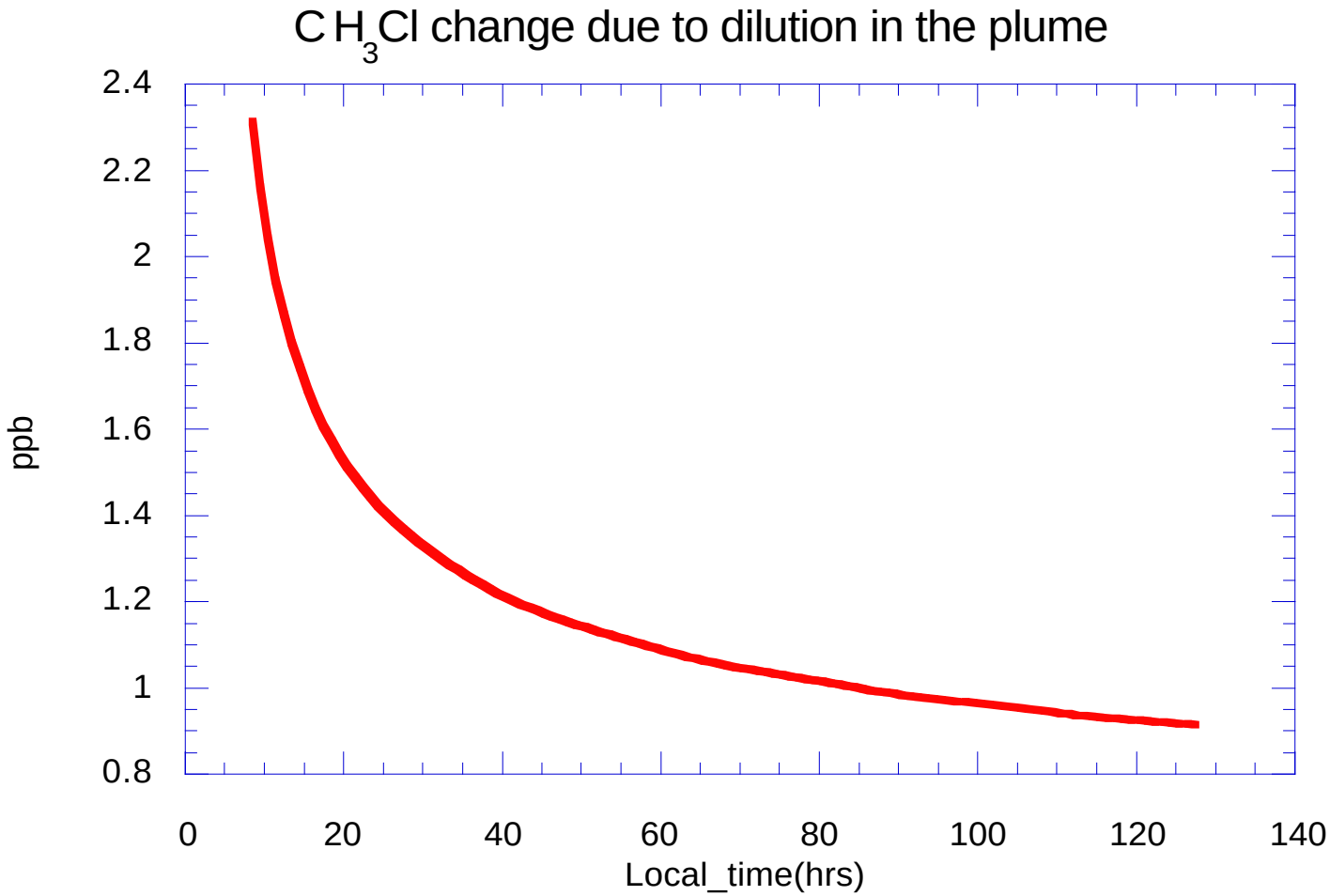
- The plume was assigned an initial width of 90 km (the size of the grid in the MM5 simulation used for making the trajectories).
- Plume then assumed to grow as a function of time with coefficients derived from Walton and Gelinas(1979) and Gifford(1984).
- The final width of the plume after 5 days is approximately 500 km.

Assumed path and width of the plume for the lagrangian trajectory photochemical calculation. The green lines represent the width of the plume during the five day period. The plume width at the origin was assumed to be 90 km.

Initial conditions for trace gases

- The measured mixing ratio of Ch3Cl in Phoenix were used to constrain the initial mixing ratios of Ch3Cl in the plume.
- The calculated mixing ratios of Ch3Cl at the origin of the plume were then used to derive mixing ratios of hydrocarbons, ozone and NOx at the plume origin using correlation's available in the literature for biomass plumes.
- A number of calculations were then performed to iteratively improve the initial conditions of Ch3Cl and hence the other trace gases.

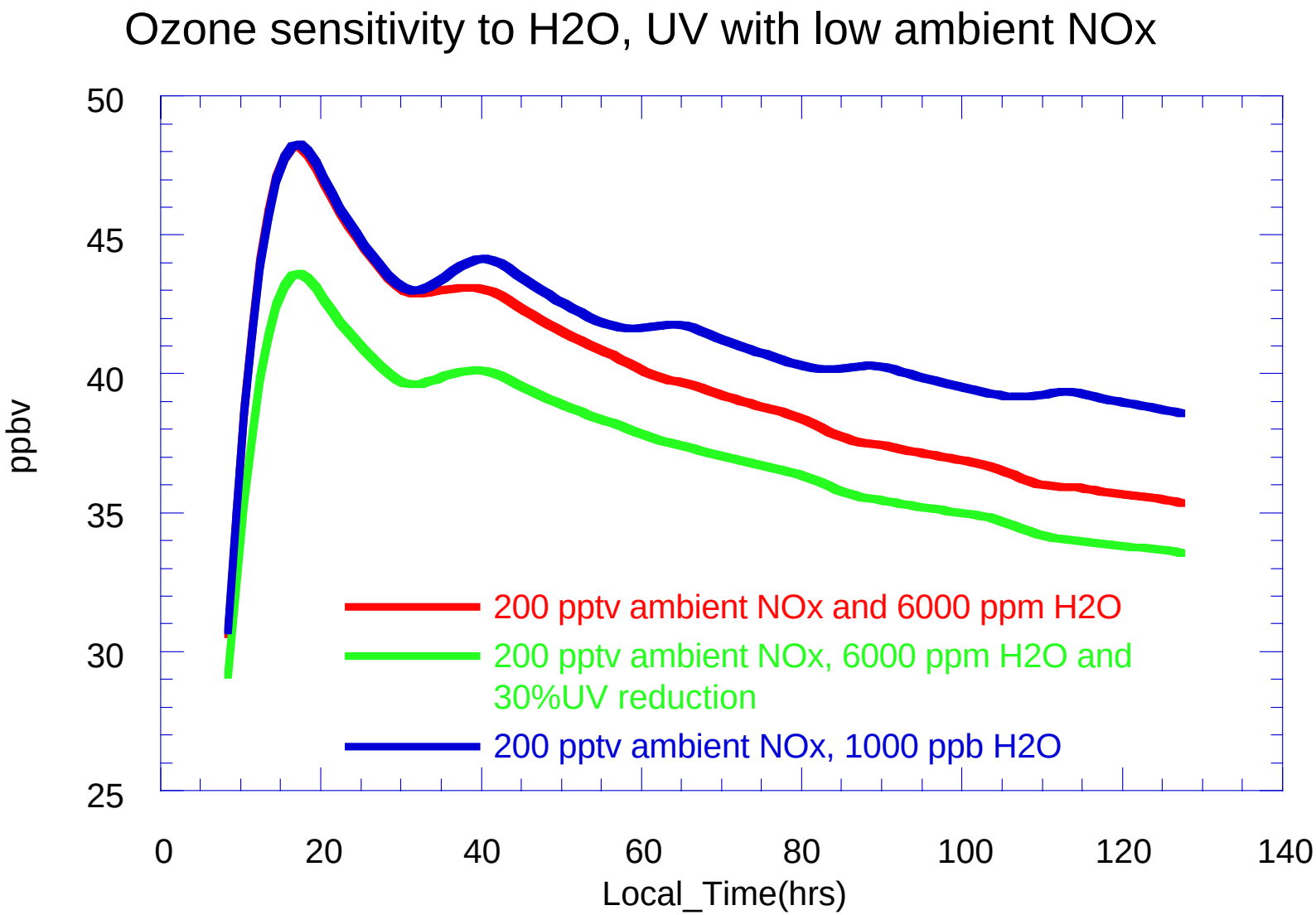
Calculated mixing ratio of Ch3Cl at the plume origin with the measured constraint of 900 pptv at the end of the trajectory



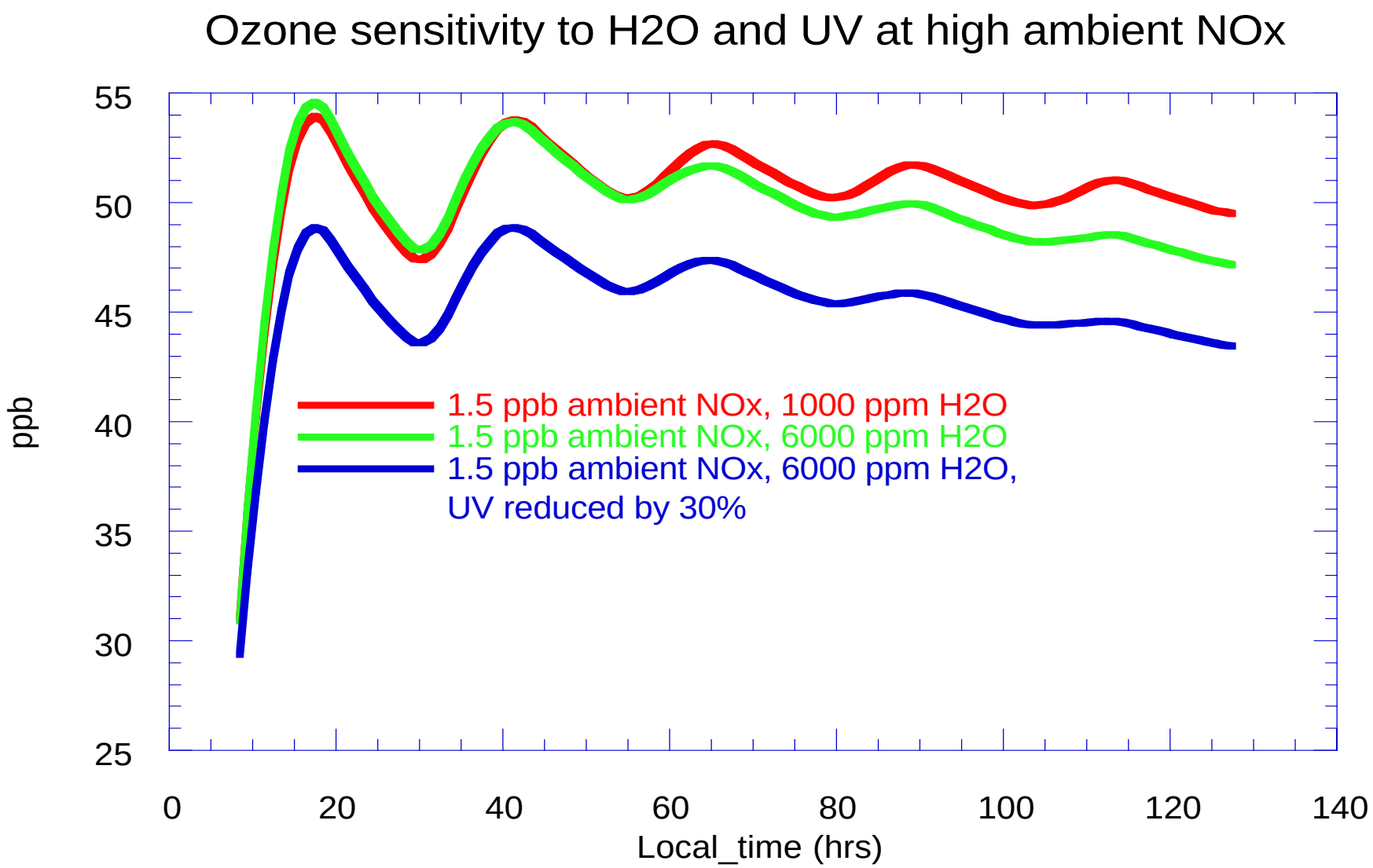
Questions addressed here

- Is the air observed at Usery pass on May 20 really originate from near the forest fire locations in Mexico.
- What explains the low ozone
- What does the high peroxide levels do the Ox chemistry
- Does the reduction in UV effect ozone production and mixing ratios.

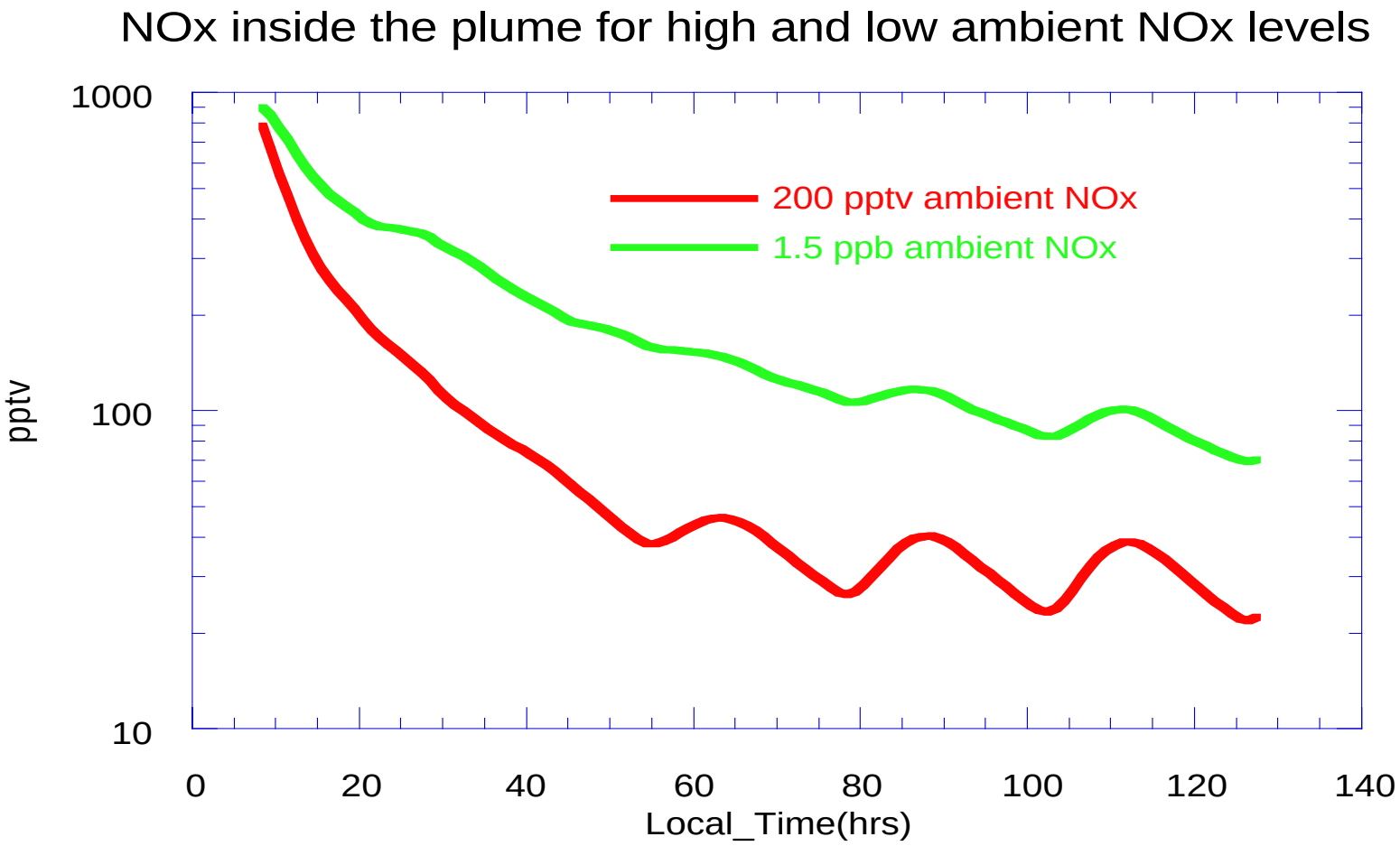
Calculated sensitivity of ozone to water vapor and UV for low ambient NOx conditions. The plume is allowed to entrains trace gases from the ambient.



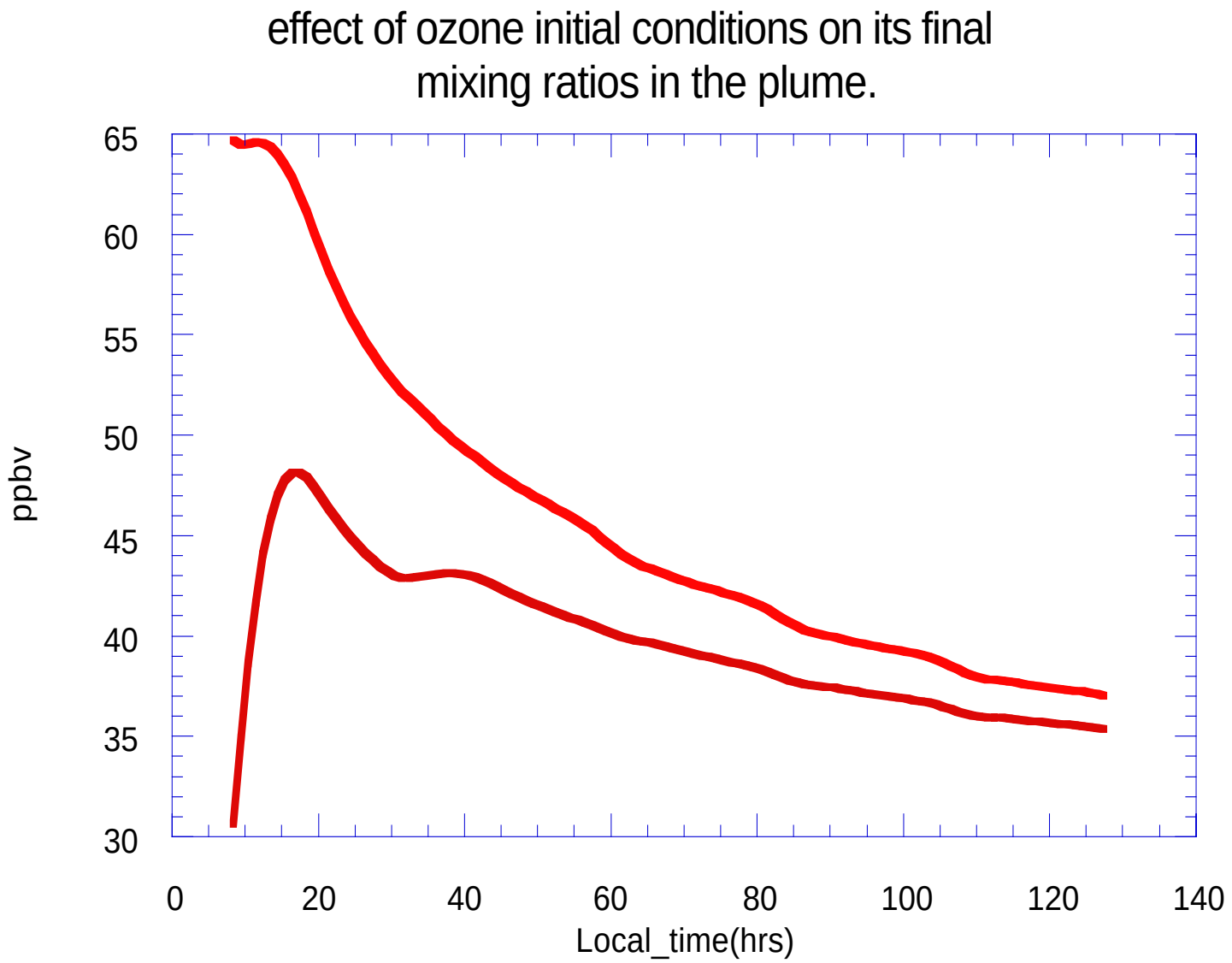
Sensitivity of calculated ozone in the plume for high ambient NOx conditions to water vapor and UV.



Mixing ratio of NOx inside the plume for the two ambient NOx cases used in the calculations.



Effect of ozone initial conditions on the calculated mixing ratios of ozone at the end of 5 days.



Conclusions

- The boundary layer air observed on May 20 has its origins in the regions were the forest fires were observed from satellite measurements.
- The low ozone is due to increased ozone loss from HO2 and the rapid decrease of NOx in the plume. High ambient NOx of the order of 1.5 ppb allowed to be entrained in the plume produces about 40+ ppb of ozone at the end of five days. This would represent conditions close to the surface. With an ambient NOx mixing ratios of the order of 200 pptv (avg mixing ratios in the continental background), there was no net increase of ozone in the plume.
- Reducing UV by 30% decreased ozone levels by 10% after 5 days of plume evolution.

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